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Development of

HIGH-TEMPERATURE, HIGH-CURRENT, ALKALI-METAL, VAPOR-FILLED CERAMIC THYRATRONS AND RECTIFIERS

by

A. W. Coolidge

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-6005

GENERAL ELECTRIC

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March 23, 1965

CONTRACT NAS3-6005

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Development of
HIGH-TEMPERATURE, HIGH-CURRENT, ALKALI-METAL
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by A. W. Coolidge
General Electric Company

SUMMARY

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The purpose of the National Aeronautics and Space Administration Contract NAS3-6005 is to advance the technology and to provide fundamental design data for high-temperature, high-current, alkali-metal, vapor-type ceramic tubes. The objectives of this program are to conduct a fundamental investigation of the problem areas associated with high-temperature, vapor-type tubes, and to fabricate and test prototype rectifiers and thyratrons to prove the technology and to provide application data for future reference. Phase I of this program is concerned with the investigation of the fundamental problems and the establishment of the conceptual design of prototype models.

During the reporting period, work was completed on devices filled with alkali halides. In addition, cesiated cathode emission was studied with respect to the relation between tube drop and cathode temperature. Also the evaluation of inverse anode current was continued. Hafnium coated and zirconium-carbide coated anodes are compared to bare molybdenum anodes and rubidium vapor is compared to cesium.

Consideration is given to materials other than cesium that might provide a suitable vapor pressure and low arc drop for high-temperature tubes. Finally the use of thoriated tungsten as a cathode material for high-temperature tubes is discussed.

Author

INTRODUCTION

Testing has been completed on devices filled with cesium iodide. A brazing alloy of palladium and cobalt demonstrated superior resistance to attack from exposure to cesium-iodide vapor. Cathode emission was observed in the device although the tube drop was high.

Two new anode materials, hafnium and zirconium carbide, were compared to molybdenum with respect to inverse emission characteristics. A tube was made with a rubidium fill instead of a cesium fill. Although the (rubidium) tube drop was higher, the inverse anode-voltage limitations were practically identical to those for cesium-filled tubes.

Three thallium-filled devices were built. A fair evaluation of thallium, however, has not been made because of mechanical problems in the devices.

A thoriated-tungsten feasibility tube has been designed and a sample is presently under construction.

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

PUBLICATIONS - None

LECTURES - None

REPORTS

1. Monthly Progress Report No. 5
   Period Covered: 19 December 1964 through 18 January 1965
   Author: A. W. Coolidge

2. Monthly Progress Report No. 6
   Period Covered: 19 January 1965 through 18 February 1965
   Author: A. W. Coolidge

CONFERENCES

1. Organizations represented
   National Aeronautics and Space Administration
   E. A. Koutnik
   Missile Space Division, General Electric Company
   R. Edwards
   Microwave Tube Business Section, General Electric Company
   E. A. Baum
   A. W. Coolidge
   A. Michaelson
   R. P. Watson
   Place and date: General Electric Company, Schenectady, New York, December 17, 1964
   Subject: Review technical progress on this project

2. Organizations represented
   National Aeronautics and Space Administration
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Microwave Tube Business Section, General Electric Company

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A. W. Coolidge

N. D. Jones

A. Michaelson

D. L. Schaefer

Place and date: General Electric Company, Schenectady, New York, February 8, 1965

Subject: Review technical progress on this project.

TECHNICAL DISCUSSION AND PROGRESS

ALKALI HALIDES

Testing was completed on two Z-7009 tubes (5 and 6) filled with cesium iodide. Tube 5 was fabricated with Palco (palladium-cobalt) brazed seals while tube 6 was fabricated with nickel-titanium brazed seals, the seal area being covered by a layer of nickel plating.

Tube 5 was subjected to four temperature cycles over a period of a week. The initial impedance across the tube was greater than 20 megohms. The impedance of the tube always decreased as the temperature was increased (it is felt that this apparent change in impedance was caused by a slight thermionic converter action, since a negative voltage as high as 0.4 volt open circuit appeared at the anode). Some cathode emission was observed, although only with a high tube drop of about 50 volts at 5 amperes peak. The cold impedance of the tube at the present time is 1.3 megohms. While this is a significant reduction from the original impedance, it is several orders of magnitude better than comparable tubes made with nickel-titanium brazing compound.

Nickel plating was found to be inadequate in protecting against formation of a halogen cycle in the presence of nickel-titanium brazing compound. Although the cold impedance of tube 6 was initially 18,000 ohms, the impedance fell precipitously during test to a fraction of an ohm.

CESIATED CATHODE EMISSION

The previous quarterly report gave data on arc drop versus current for the Z-7009 tubes 2 and 3. Both tubes, which were of the design shown in Figure 1, contained a molybdenum cathode and cesium fill. Cathode temperature varied from 1150 to 1450°C and, indeed, at the higher cathode temperatures there was enough thermionic converter action to cause the arc drop to be negative.

On another Z-7009 (tube 7) of similar design (except for its anode surface which will be discussed in a later section), cesiated emission data was taken over a range of cathode temperatures that extended downward until the tube drop increased to more than 10 volts, Figure 2. It can be

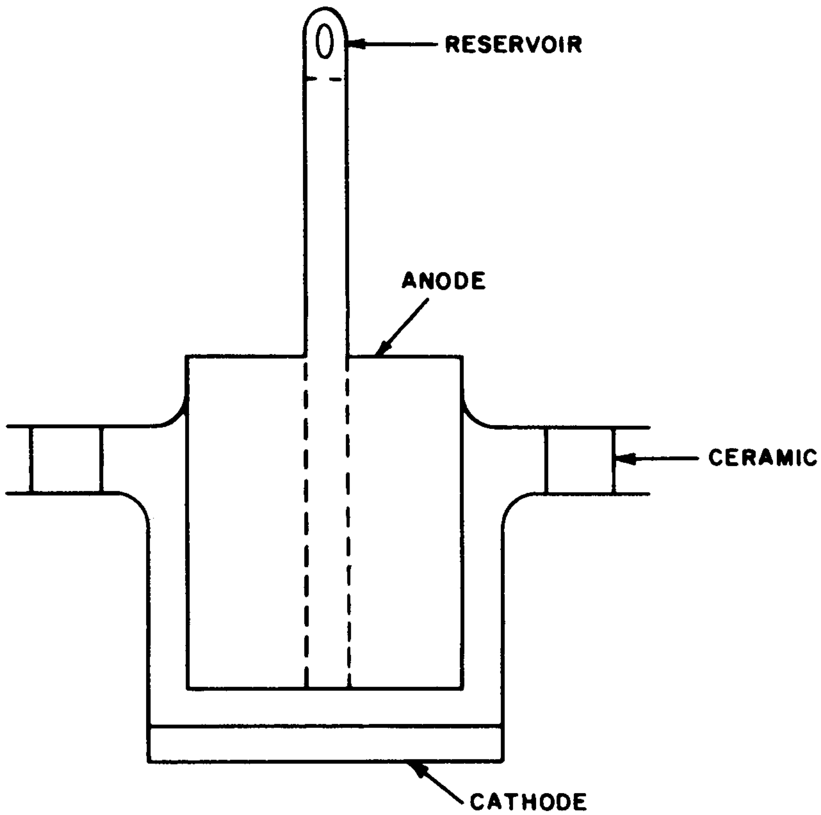

Figure 1 - Schematic of Test Vehicle, Design A

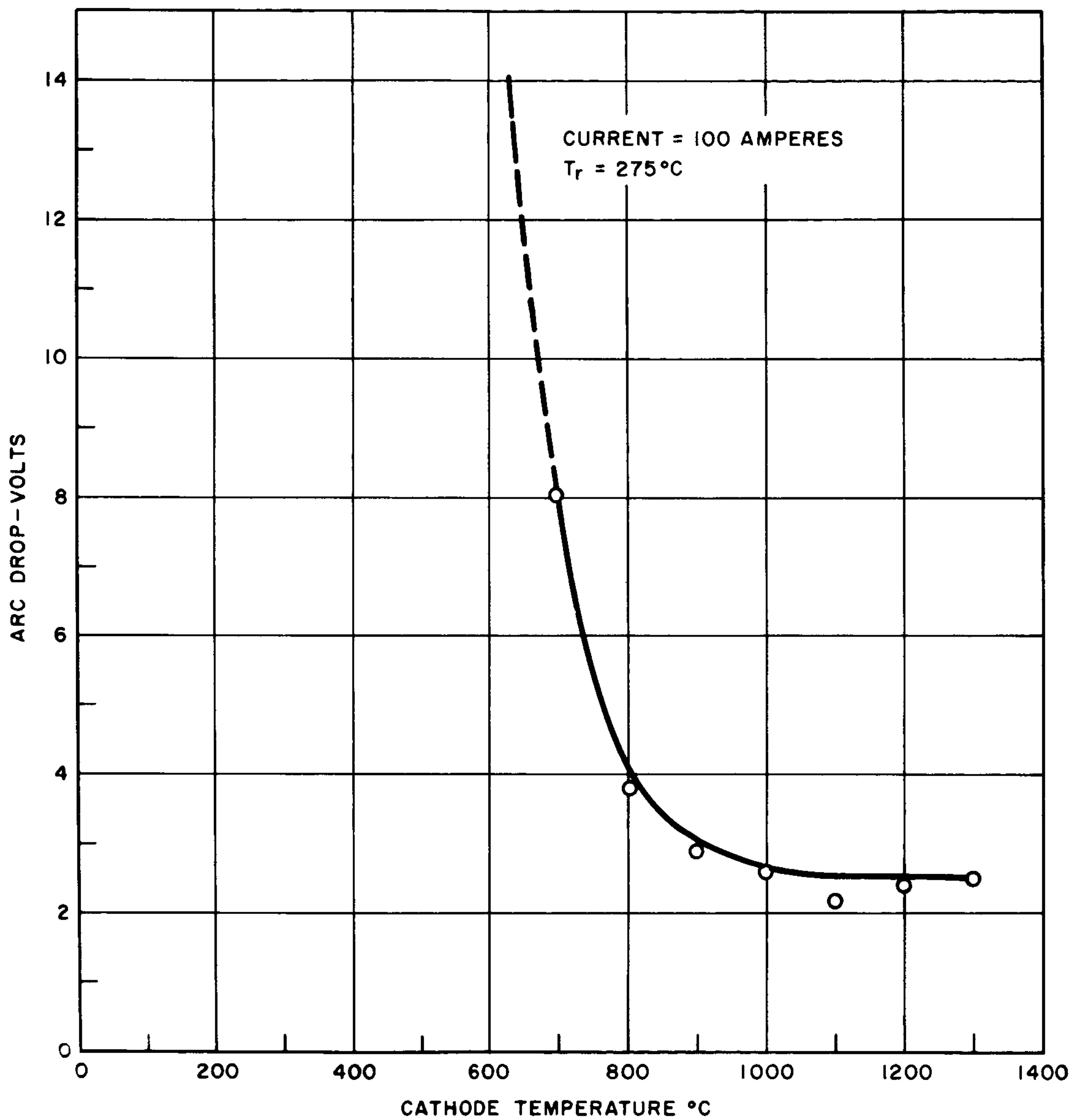

Figure 2 - Peak Drop versus Cathode Temperature, Z-7009 Tube 7

seen that there is little change in tube drop as the cathode temperature is lowered from 1300 to 900°C. Thus, from the standpoint of efficiency it would be wasteful to provide the extra power needed to heat the cathode to a temperature of 1200 to 1300°C.

A reasonable analysis of efficiency may be made by

1. Measuring the relation of heater power to cathode temperature, which constitutes an external power loss

2. Calculating an internal power loss from the curve of Figure 2, multiplied by an assumed average current of fifteen amperes (the Phase I current level objective)

3. Obtaining the total power loss which is equal to the sum of the internal and external losses.

Figure 3 exhibits, as a function of cathode temperature, the component and total losses. As can be seen from Figure 3, the most efficient point of operation occurs at a cathode temperature of 800°C. In practice, it would probably be best to operate the cathode at about 900°C. This would allow for variations between tubes, as well as for electron cooling at the cathode, which produces a power loss of I_b (W.F. + 2KT/e)

where W.F. = work function of the cathode in volts

K = Boltzman constant

= 1.3708×10^{-23} watt-second/degree K

T = cathode temperature in degrees K

e = charge of electron = 1.590×10^{-19} coulomb

Since the 2KT/e term is only about 0.1 volt in magnitude, it may be neglected without serious results, yielding I_b(W.F.) as the approximate power loss due to electron cooling.

GRID AND INVERSE EMISSION

Successful thyratron operation requires that the grid emission and the anode emission be held to low values. If one or the other element is not a poor emitter, the tube will not hold off voltage in the forward or the

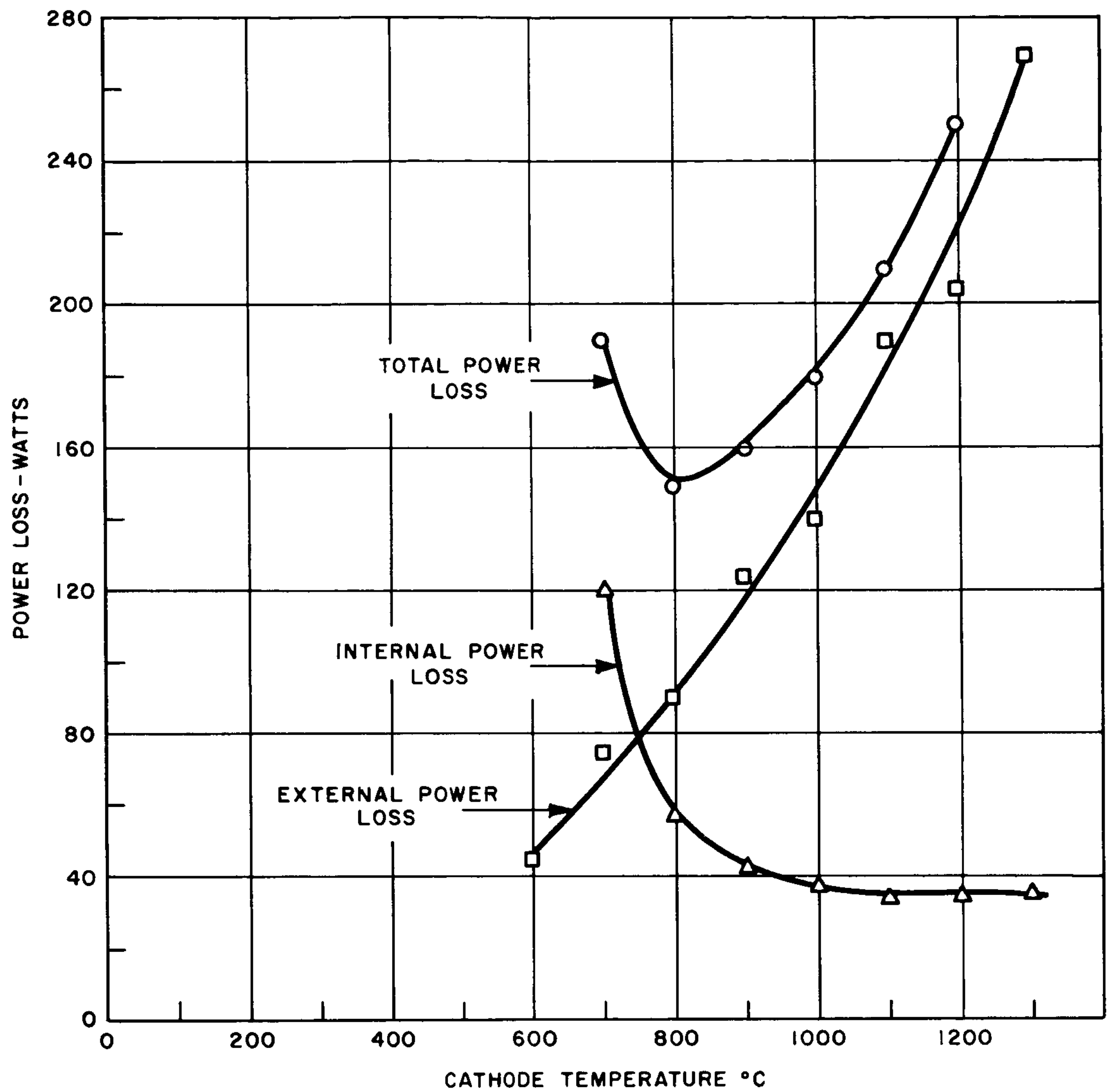

Figure 3 - Power Loss versus Cathode Temperature, Z-7009 Tube 7

reverse direction. The critical current for breakdown is a function of tube design and the impressed voltage across the tube. In the cesium-filled tubes studied, there are indications that the tube will not be capable of holding off 1000 volts inverse if the anode is capable of emitting as much as a fraction of a microampere per square centimeter.

The second quarterly report discussed the effect of the substrate work function on the work function of a cathode covered with a thin layer of cesium. As shown in Figure 4, a substrate material having a work function of 3.0 would appear to be the best material for an anode or a grid.

Two new anode materials having work functions near 3.0 were chosen for evaluation and were studied. These materials, zirconium carbide and hafnium, were applied to molybdenum anodes by means of a plasma spraying process.

The Z-7009 tube 7 contained the zirconium-carbide anode and was of Design A, Figure 1. The relation of inverse voltage to anode temperature is given in Figure 5; the improvement over bare molybdenum was negligible. It was noticed during test, however, that breakdown was occurring between the tantalum seal flanges inside the tube. Because the anode flange temperature is essentially the same as the anode temperature and because tantalum has a high work function, as does molybdenum, it is possible that zirconium carbide did not receive a fair test in tube 7.

To guard against spurious breakdown between seals, tube 14 was made with a thin alumina wafer guard ring (Figure 6). The inner diameter of the guard ring was just a few mils larger than the anode diameter. Test results on tube 14 (Figure 7) were even poorer than those of tube 7.

The Z-7009 tube 8 was identical in design to tube 14, except that the anode was coated with hafnium. A degradation in inverse-voltage capability, as a result of thermal emission, occurred at an anode temperature of 410°C, Figure 8. This compares with a corresponding anode temperature of 380°C for the case of an uncoated molybdenum anode. Tube 8 was studied through a cesium reservoir temperature range of 300 to 125°C, corresponding to a pressure range of 1200 to 3 microns. At the low end of the range, there was an improvement in the inverse-voltage characteristic, since 560 volts inverse could be sustained at an anode temperature of 620°C. This is of academic interest only since the cathode emission is restricted to very low current levels when the cesium pressure is low enough to permit this gain.

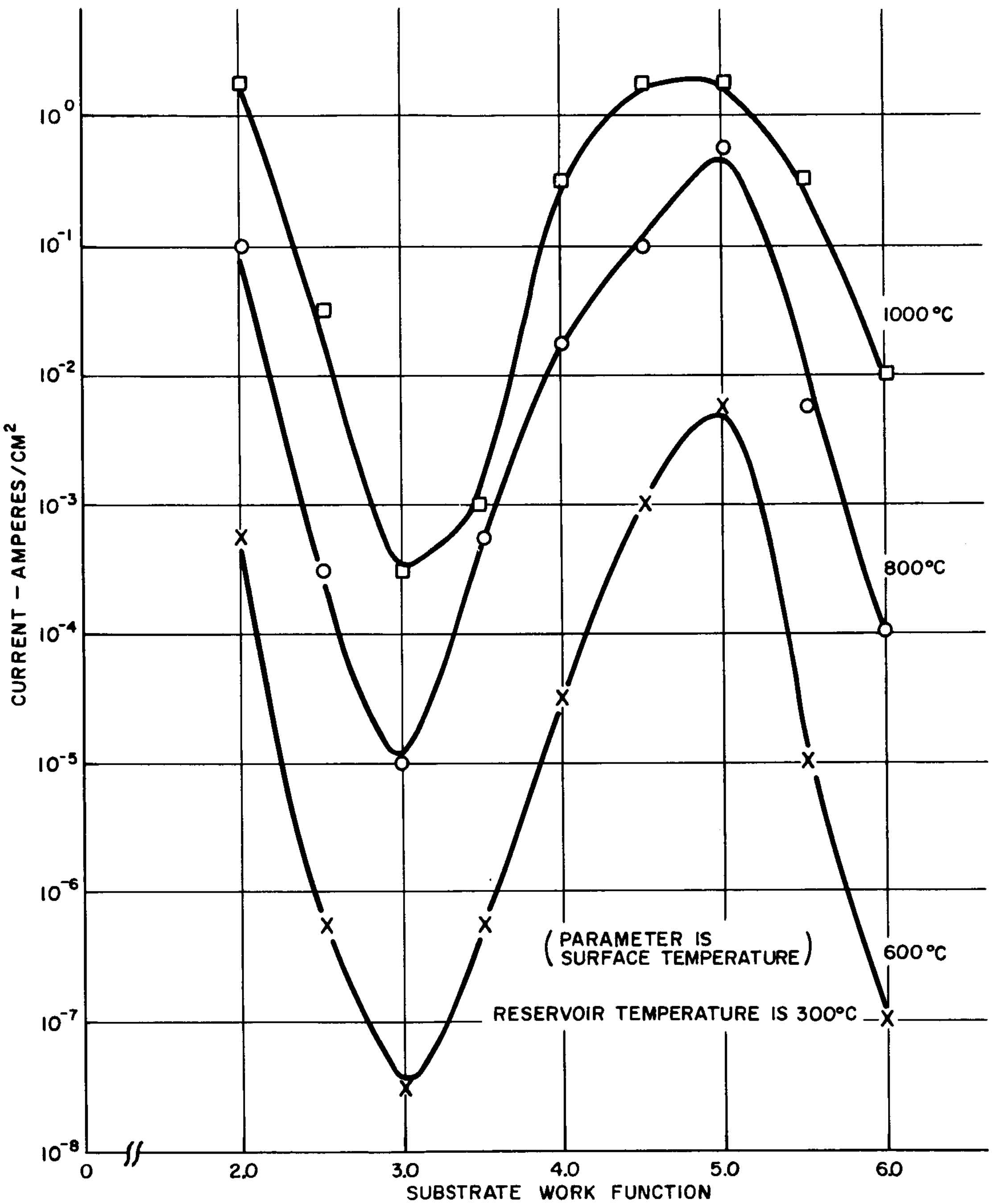

Figure 4 - Cesiated Emission versus Substrate Work Function

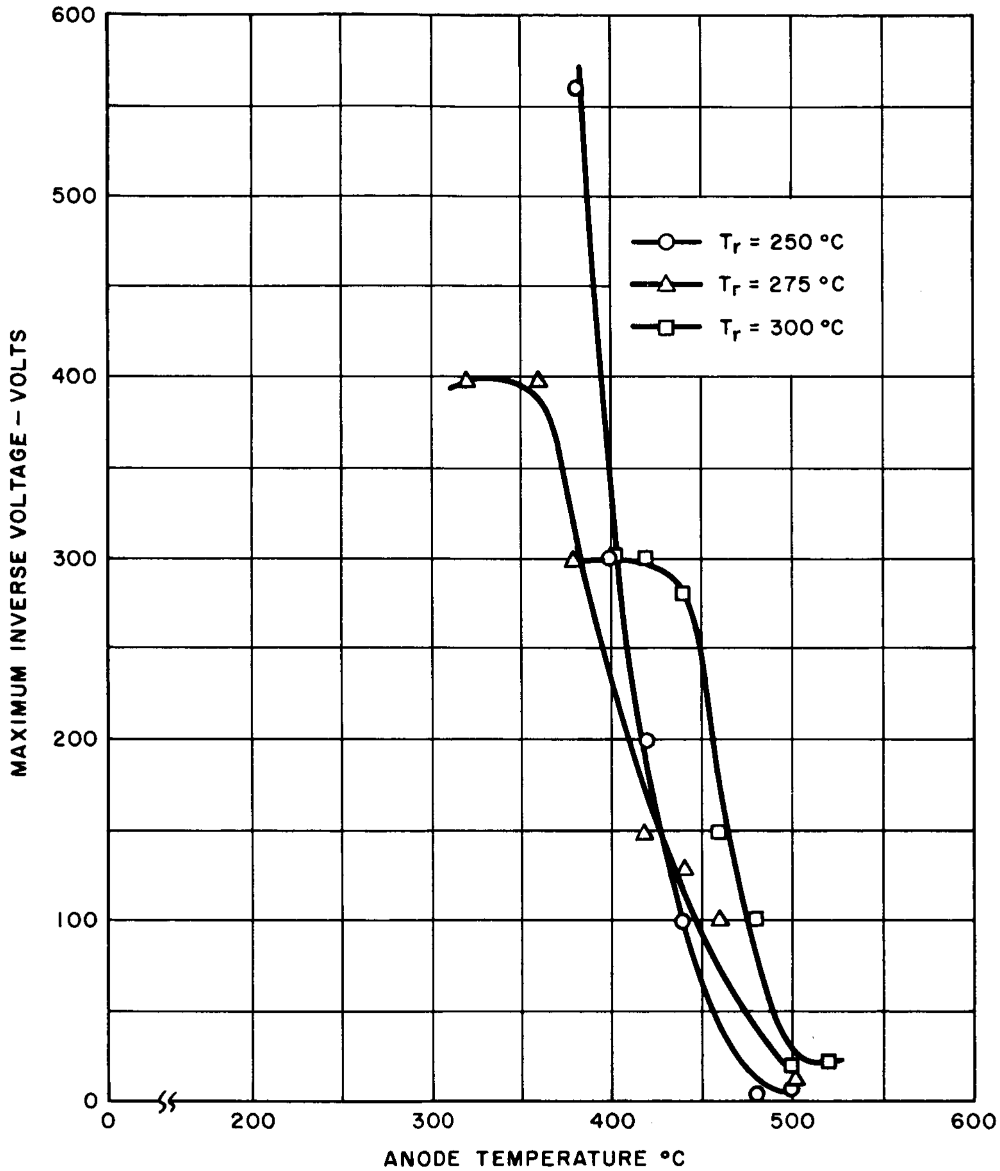

Figure 5 - Maximum Inverse Voltage Without Breakdown versus Anode Temperature, Z-7009 Tube 7

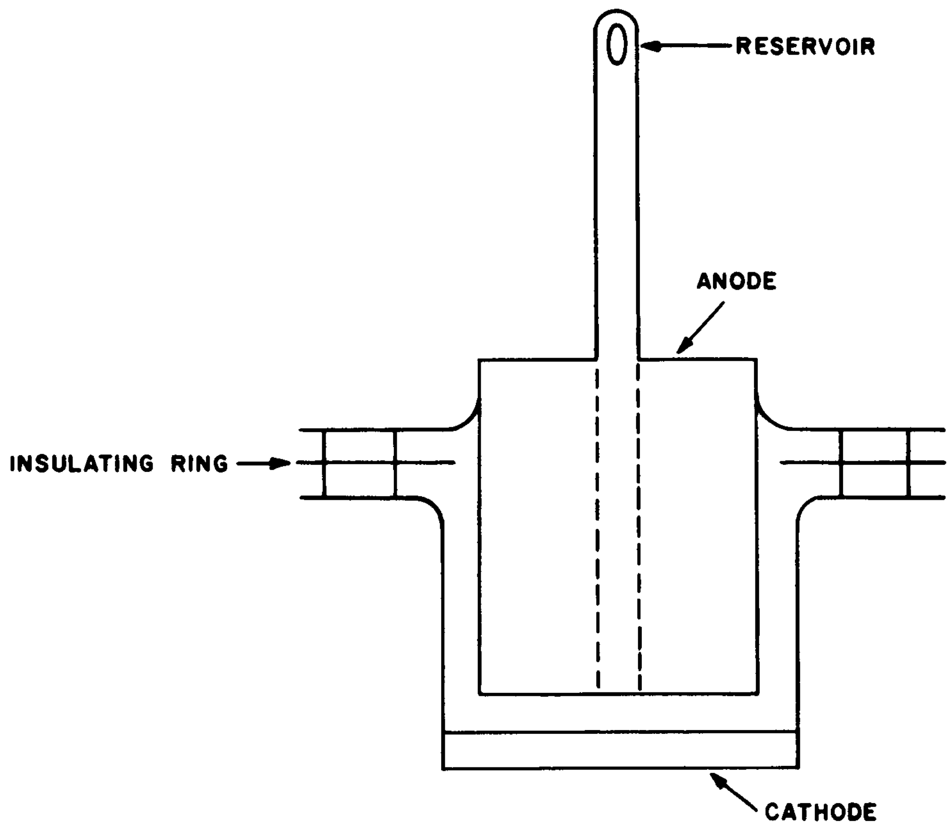

Figure 6 - Schematic of Test Vehicle, Design D

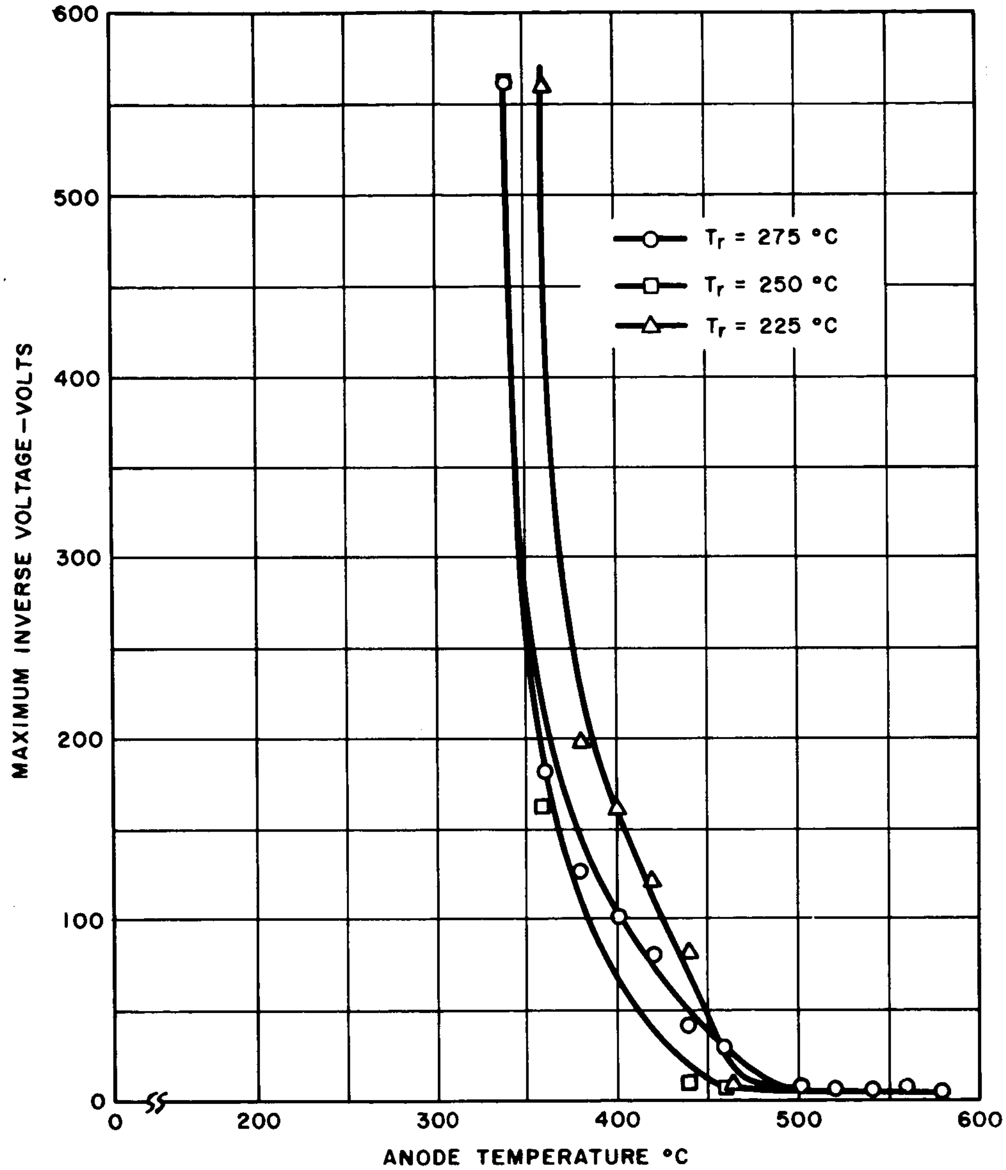

Figure 7 - Maximum Inverse Voltage Without Breakdown versus Anode Temperature, Z-7009 Tube 14

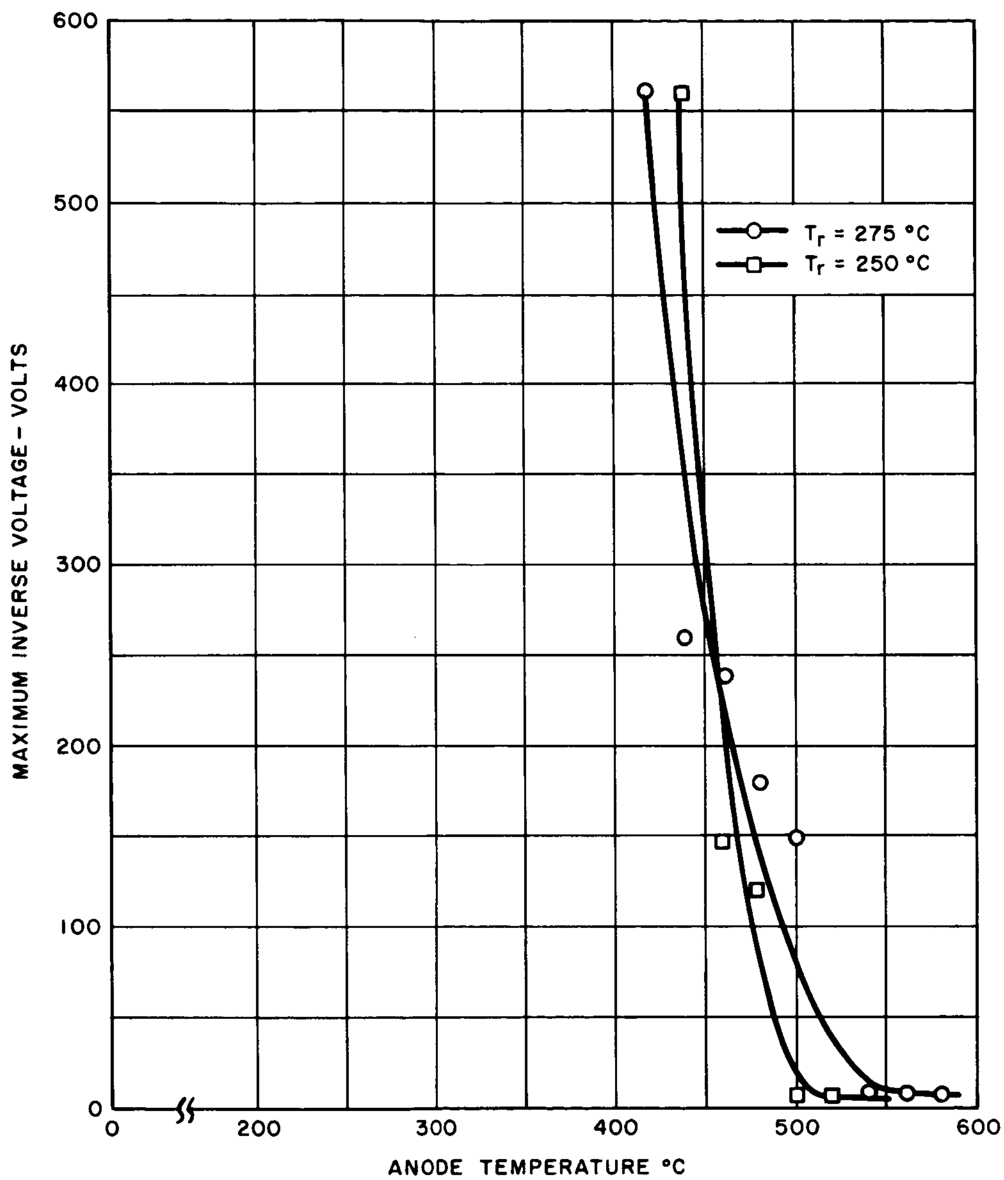

Figure 8 - Maximum Inverse Voltage Without Breakdown versus Anode Temperature, Z-7009 Tube 8

The other alkali metals, rubidium, potassium, sodium and lithium and the alkali earths barium, strontium and calcium, like cesium, have the capacity, of lowering the work function of a substrate material when they are deposited on the substrate in the form of a thin film. Because cesium has the lowest work function and the lowest ionization potential of all the alkali metals, it was felt that a different alkali metal might produce a less efficient emitter and result in a tube whose anode emission was lower at a given temperature. This presented the possibility of coupling a less efficient cathode with an anode that could be raised to a higher temperature before the advent of inverse voltage breakdown.

The Z-7009 tube 15 was made with a rubidium fill and yielded the emission versus reservoir temperature and the cathode temperature data shown in Figures 9 and 10, respectively. A comparison between Figures 2 and 10 indicates that the rubidium tube has less efficient cathode emission but its inverse-voltage characteristic (Figure 11) is not improved over that obtained with a cesium-fill tube. Because of these results, no further work is planned with rubidium or with any of the other alkali metals.

Sufficient data is available for estimating the maximum ambient or heat-sink temperatures to which alkali-vapor tubes might be used. The maximum heat-sink temperature is considered to be the maximum permissible electrode temperature less the thermal drop between the electrode and the heat sink. For a structure of the type shown in Figure 12 and for the case of a 15-ampere tube, where anode dissipation might be in the order of 100 watts, it was computed that the thermal drop could be held to about 100°C. Thus the maximum heat-sink temperatures for the various combinations of anode and fill material studied are given below and summarized in Figure 13.

Combination	Heat-Sink Temperature (°C)
1. Molybdenum anode, cesium fill	280
2. Zirconium carbide anode, cesium fill	240
3. Hafnium anode, cesium fill	310
4. Molybdenum anode rubidium fill	240

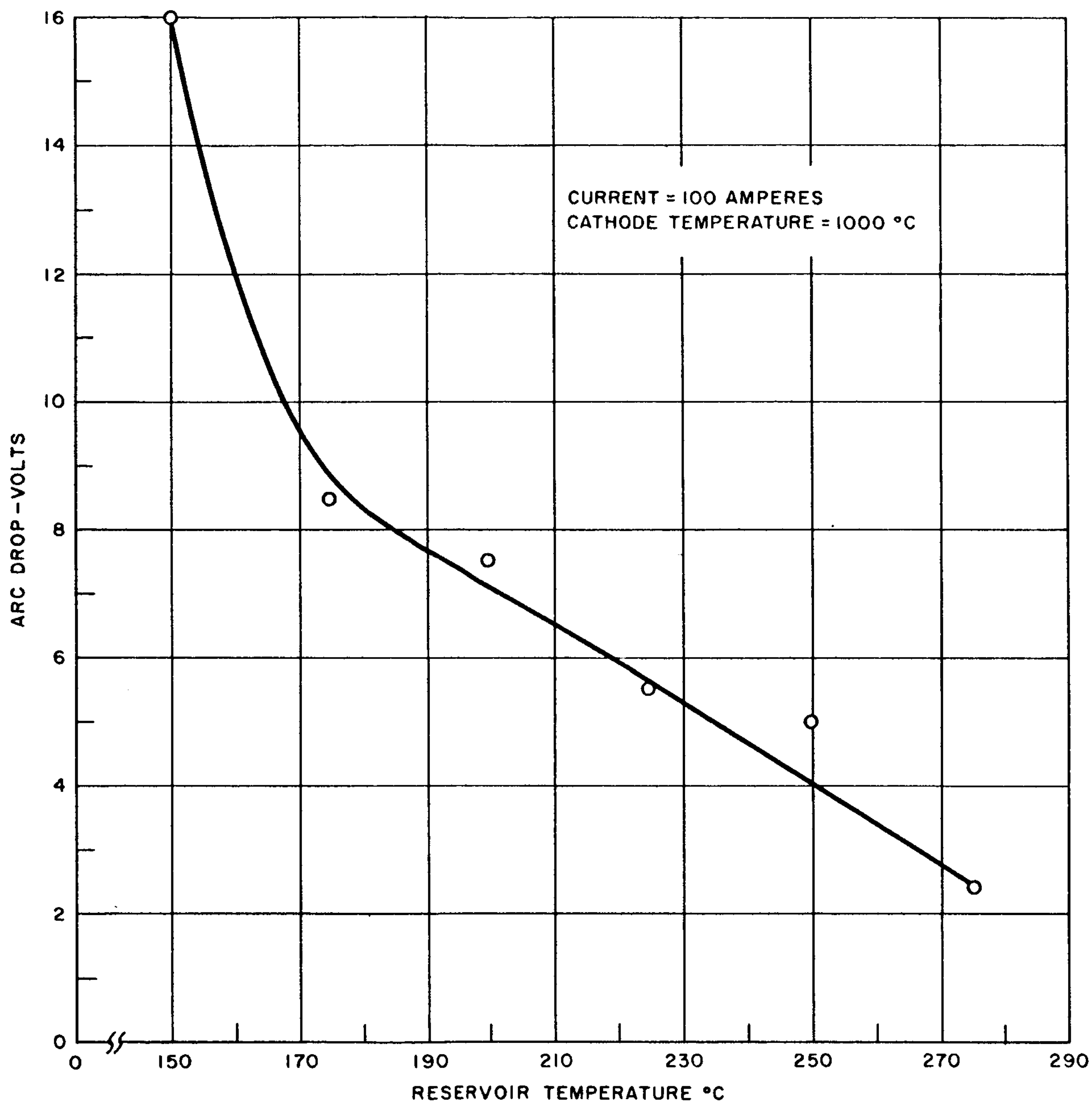

Figure 9 - Peak Drop versus Cathode Temperature, Z-7009 Tube 15

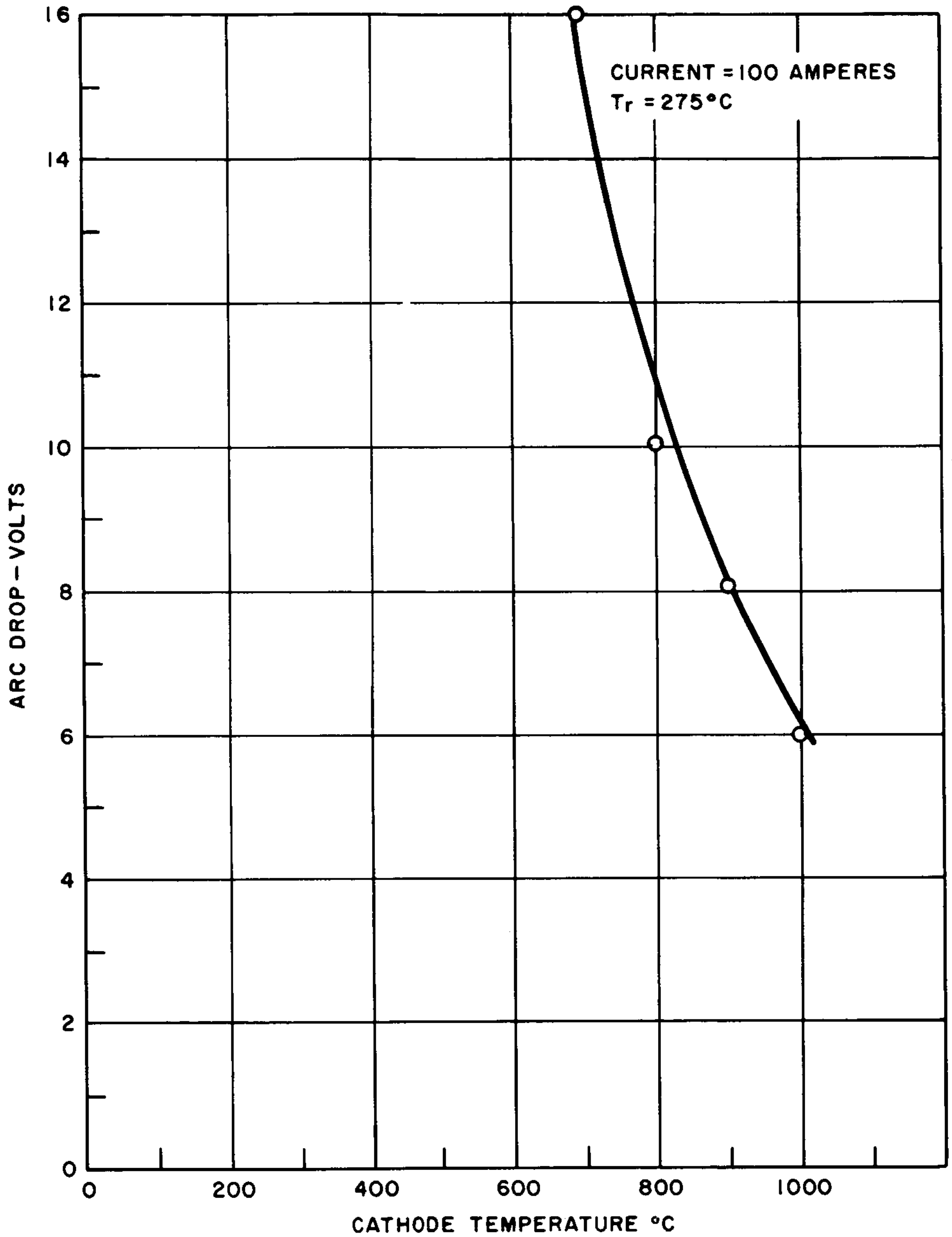

Figure 10 - Peak Drop versus Cathode Temperature, Z-7009 Tube 15

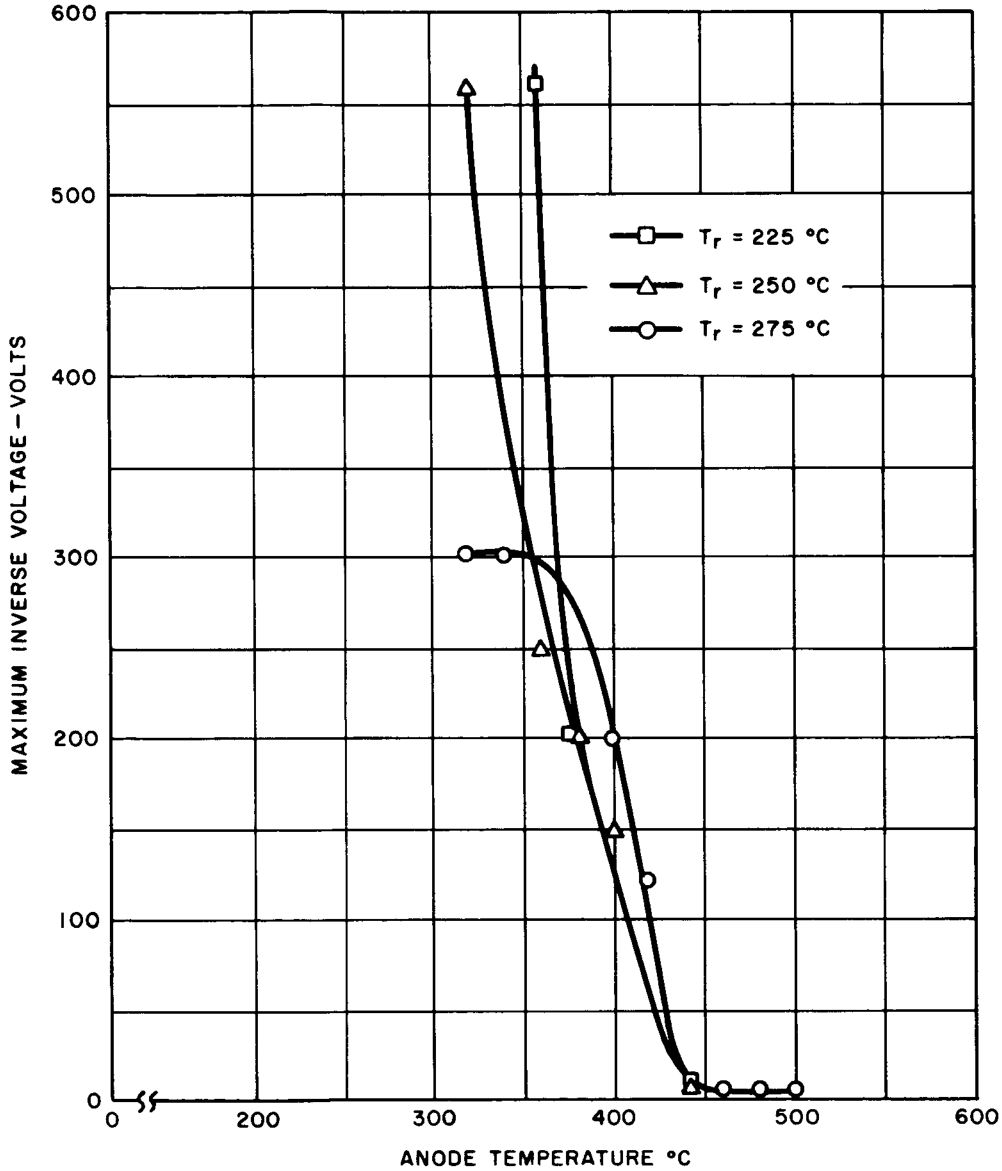

Figure 11 - Maximum Inverse Voltage Without Breakdown versus Anode Temperature, Z-7009 Tube 15

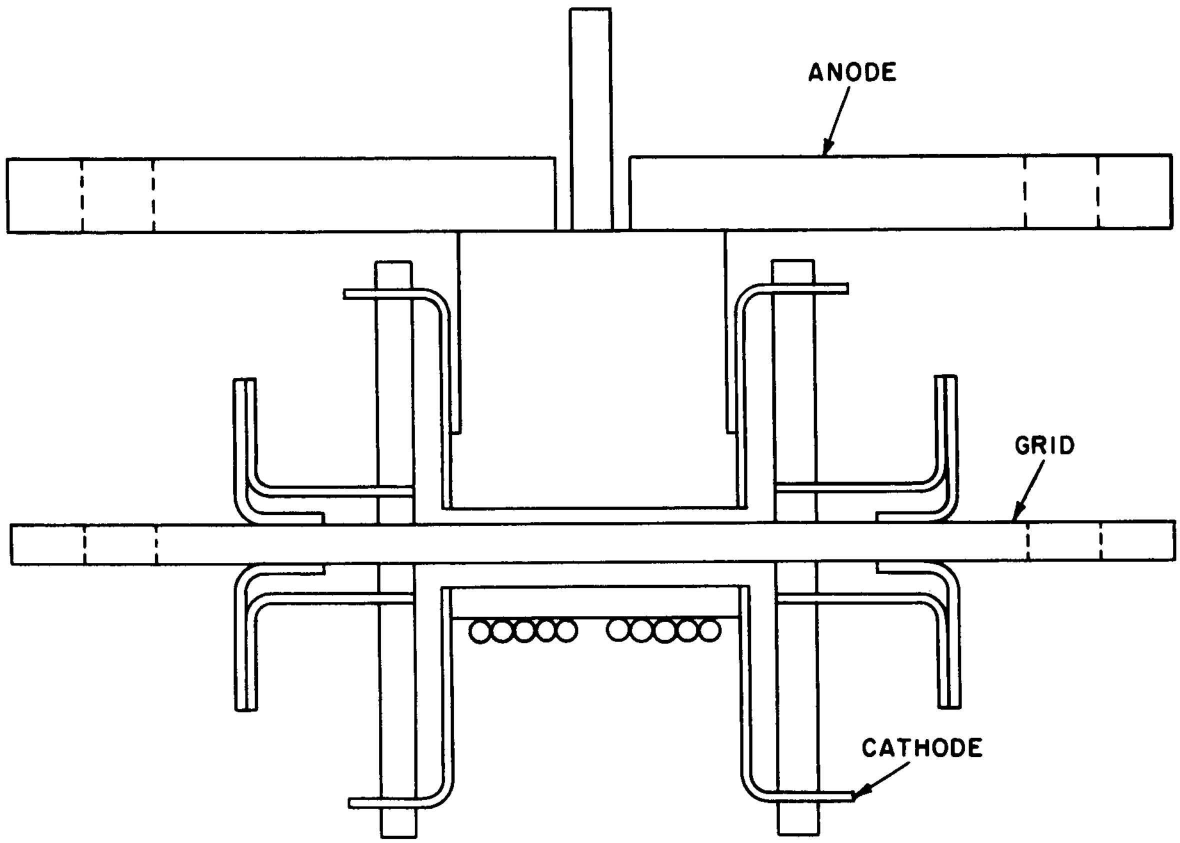

Figure 12 - Conceptual Design for High-Temperature Thyratron

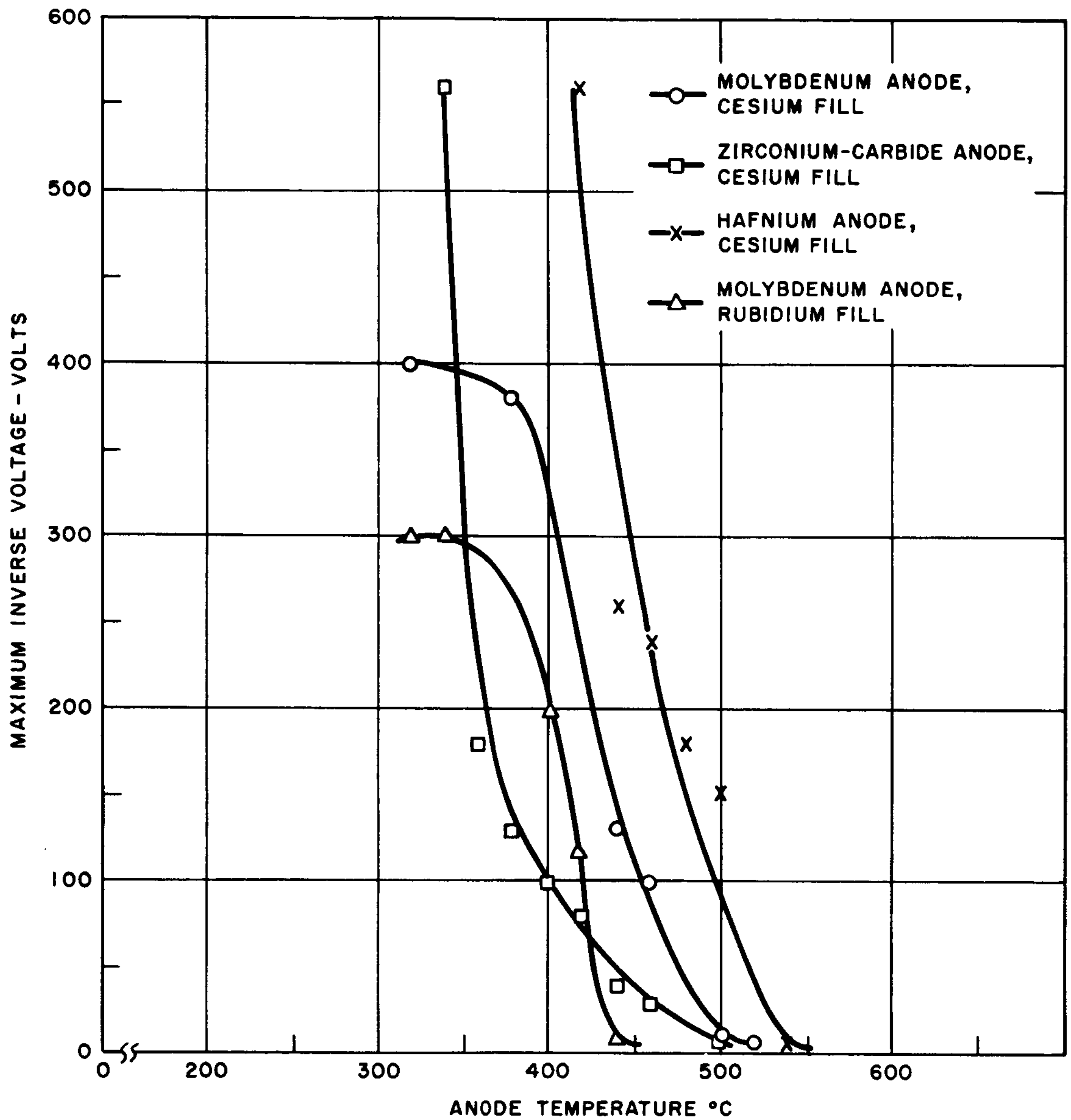

Figure 13 - Maximum Inverse Voltage Without Breakdown versus Anode Temperature for Various Anode and Fill Combinations

Because the preceding heat-sink temperatures are so far removed from the objective heat-sink temperature of 600°C, it appears necessary to resort to a prepared cathode with lower efficiency, such as a barium or thoriated-tungsten cathode, and a fill material other than an alkali metal. These aspects are discussed in later sections.

OTHER VAPOR-FILL MATERIALS

In seeking potentially useful vapor-fill materials other than the alkali metals or compounds, the prerequisite condition is that the material under consideration must have a vapor pressure between 10^{-2} and 1 Torr in the temperature range of 600 to 800°C. Four potential materials are shown in Figure 14. Two other important requirements for these materials are ionization potential and compatibility. The ionization potentials for the elements depicted in Figure 14 are as follows:

Thallium	6.1 volts
Lead	7.4
Bismuth	8.0
Antimony	8.5

In each case, the tube drop is expected to be about a volt higher than the ionization potential.

The compatibility of the above metals with other materials commonly used in high-temperature tubes cannot be completely predicted. Phase diagrams or the constitution of binary alloys (insofar as such information is available) can be used as a guide to the compatibility problem but, as in the case of cesium, actual compatibility cannot be established without long-term testing.

Three attempts have been made to build a thallium-filled tube with a barium-system cathode but no test data has been gained because of accidents to two tubes and an incompatibility problem in the third tube.

The Z-7009 tube 10, which was of Design C construction (Figure 15), contained a thallium reservoir in the tubulation at a point about six inches away from the anode. It is possible that the reservoir heater burned out and arced to the tubulation, since there was evidence of melting and the tube became a leaker at this point.

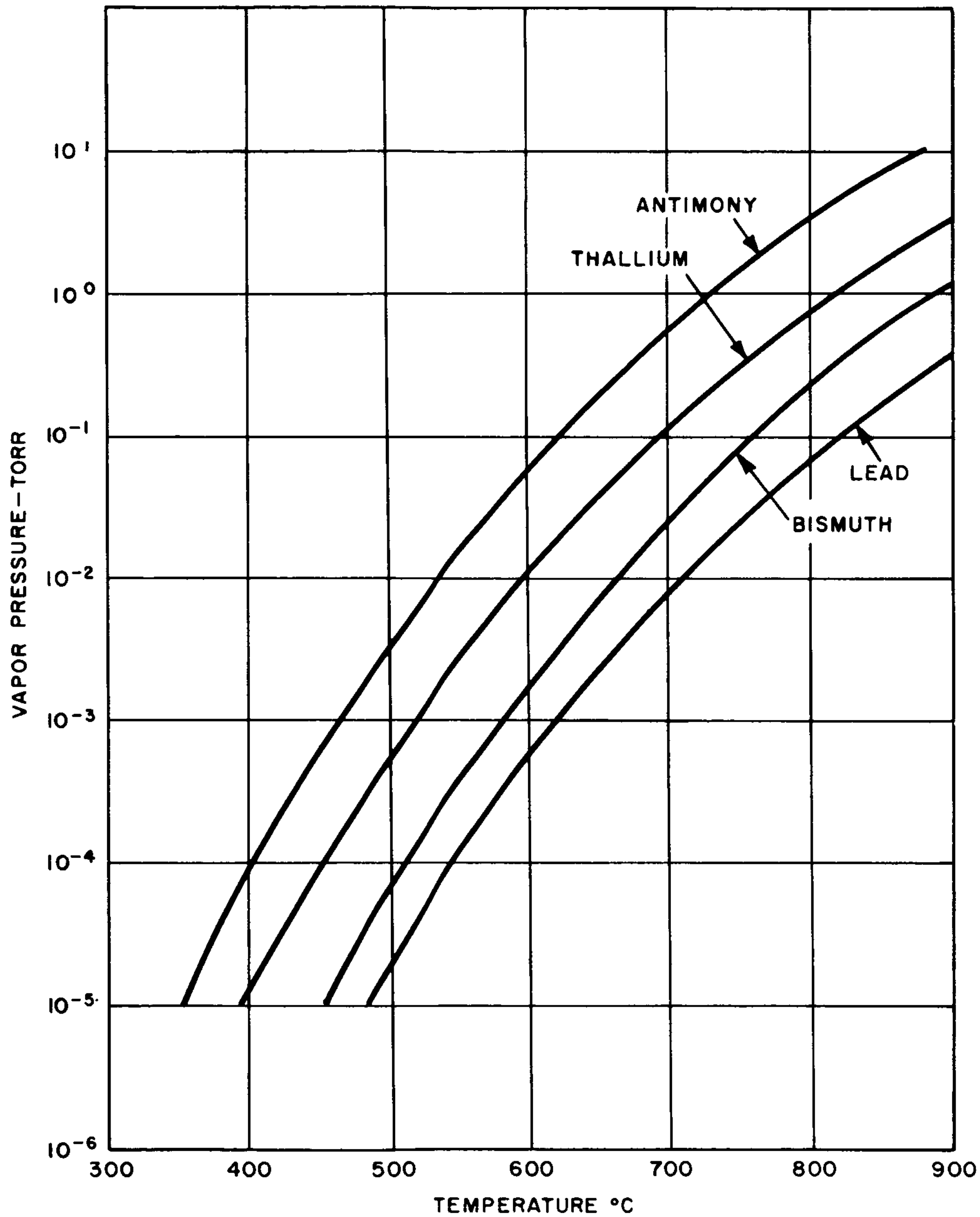

Figure 14 - Vapor Pressure Curves

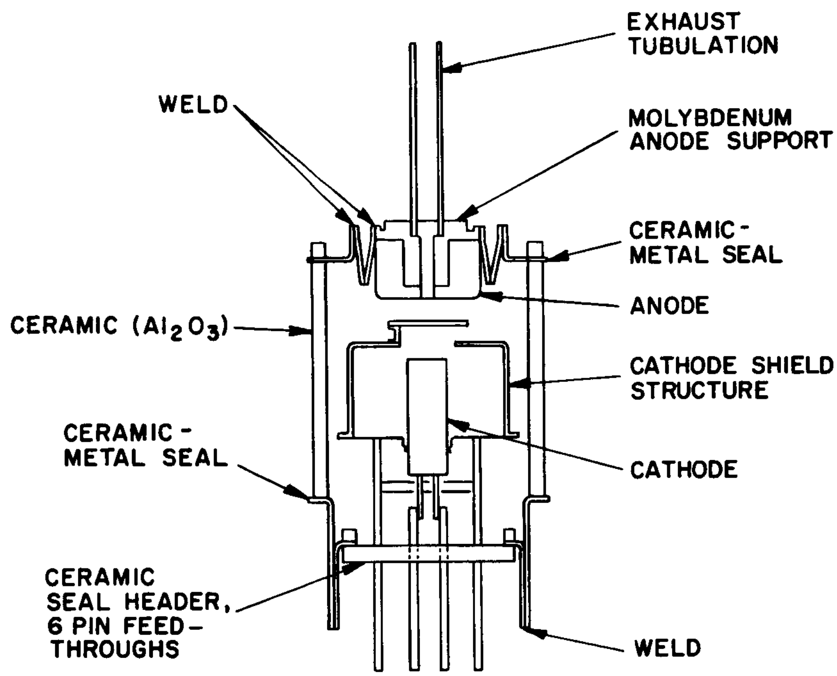

Figure 15 - Schematic of Test Vehicle, Design C

The Z-7009 tube 13 was similar to tube 10. However, in tube 13 the reservoir was located closer to the anode so that less external heating would be required to maintain the reservoir at about 800°C. This tube was successfully exhausted and pinched off, but it became a leaker because of thallium attack on the platinum conductors leading through the cathode header.

The Z-7009 tube 11 was made in accordance with Design B (Figure 16), except that the shield just inside of the ceramic insulator was omitted. The cathode was a porous tungsten disc permeated with a barium-aluminate compound. In order to prepare and age the cathode, this tube was operated on exhaust with a fill of xenon. After cooling and before pinch-off, the tube became a leaker. Subsequent inspection revealed a cracked ceramic which may have been caused by a localized breakdown during operation with xenon.

More devices are planned so that thallium and the other eligible materials may be evaluated.

CATHODE

The second quarterly report presented the following list of possible cathode and fill combinations in order of descending efficiency:

	Cathode	Fill
1.	Cesiated refractory metal	Cesium (high pressure)
2.	Barium	Cesium (low pressure)
3.	Barium	Thallium or equivalent
4.	Thoriated tungsten	Cesium (low pressure)
5.	Thoriated tungsten	Thallium or equivalent
6.	Tungsten	Cesium (low pressure)
7.	Tungsten	Thallium or equivalent

Because of the previously described temperature restrictions attending the use of alkali metals, this list may now be reduced. The remaining possible combinations of cathode and vapor fill for use in a tube in a 600°C environment are as follows:

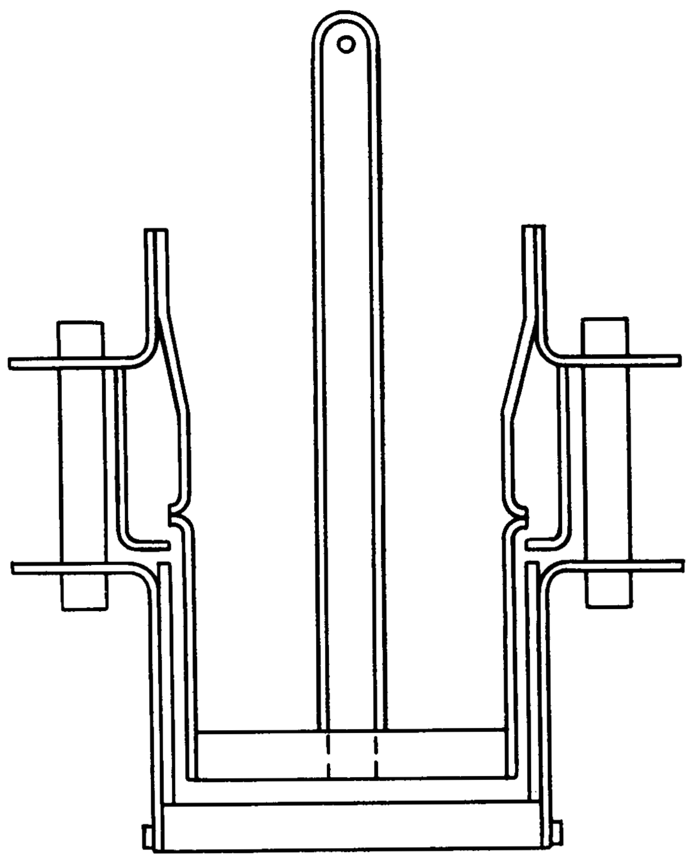

Figure 16 - Schematic of Test Vehicle, Design B

Cathode	Fill
1. Barium	Thallium or equivalent
2. Thoriated tungsten	Thallium or equivalent
3. Tungsten	Thallium or equivalent

Gas-filled tubes with barium cathodes are being studied under another contract (NAS3-6469). Tubes made with barium cathodes and graphite anodes have been operated successfully to 1200 volts inverse in an ambient temperature of 800°C. Part of the purpose of Contract NAS3-6469 is to prove that such devices may be operated with stability over periods of several thousand hours. For the barium cathode tube, a critical time arrives when enough barium has evaporated from the cathode to provide barium vapor pressure, which is determined only by the temperature of barium condensate at the coolest part of the tube. At 600°C the equilibrium barium vapor pressure is about six microns and at that pressure the rate of arrival of barium atoms at electrode surfaces within the tube is high. Thus suppression of grid and inverse anode emission will depend upon the maintenance of high work function surfaces.

Because it is not certain that a high-temperature tube using a barium cathode can be achieved successfully, and to avoid duplication of effort, it is suggested that work be concentrated on thoriated tungsten, the most efficient cathode system below barium. It is believed that ultimately both vapor and the gas tubes can use the most efficient successful cathode whether it is barium or thoriated tungsten.

As a first step in the evaluation of thoriated tungsten, a feasibility tube has been designed. This tube contains a specially designed anode that fits closely to a thoriated-tungsten cathode mounted on the bottom end of a GL-6942 transmitting tube. The anode-cathode portion of the tube, less the bottom-end supports and seals, is shown schematically in Figure 17. The cathode has an area of 2 square centimeters and is capable of about 5 amperes average current. The tube has been designed so that the anode temperature is about 1000°C when the cathode is at the normal operating temperature of 1650°C. Thus, by merely controlling the cathode temperature, the anode temperature may be controlled to any temperature below 1000°C so that a curve of maximum inverse anode voltage versus anode temperature may be established. To avoid any compatibility problem that might arise from the use of one of the metallic-vapor fills, this first tube will be filled with about 50 microns of xenon.

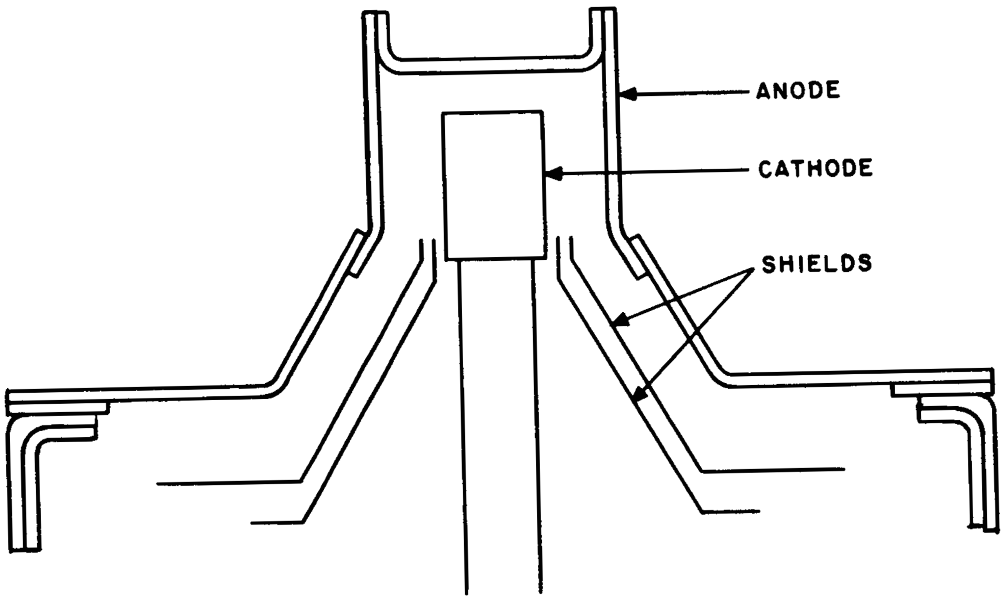

Figure 17 - Schematic of Test Vehicle, Design E

If the test results indicate voltage stability in a $600^{\circ}C$ ambient, the design of a 15-ampere thoriated-tungsten cathode will be undertaken.

PROGRAM FOR NEXT INTERVAL

During the next report period, diodes having the following special features will be assembled, exhausted and tested:

1. Thoriated-tungsten cathode with xenon fill

2. Barium cathode with thallium fill

An investigation will also be conducted in which antimony, bismuth and lead are used as fill materials.

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A. W. Coolidge

ABSTRACT

Work was completed on tubes using alkali-halides. Palladium-cobalt brazing alloy proved to be compatible with cesium iodide. Cathode emission, however, was poor.

Hafnium and zirconium-carbide were evaluated as anode materials in cesium-filled diodes and found to be essentially the same as plain molybdenum.

Rubidium was compared to cesium as a filling agent. Test data indicates that the heat-sink temperature for cesium- or rubidium-filled thyratrons or diodes should not exceed $300^{\circ}C$.

The use of (1) thoriated tungsten as a cathode material, and (2) vapor-fill materials other than alkali metals are discussed.